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Recovery of citric acid from fermented liquid by bipolar membrane electrodialysis

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ABSTRACT

The process of recovering citric acid from fermented liquid by bipolar membrane electrodialysis (BMED) was studied. Two bipolar membranes and one cation exchange membrane were stacked to form a two-compartment BMED stack configuration. The effects of the current density, initial concentration of sodium citrate, and structure of the acid compartment (AC) and base compartment (BC) on the performance of the BMED process were investigated. Filling mixed-bed ion exchange resins in BC could decrease the compartment resistance and led to a pure base solution for reuse. The highest acid recovery of 97.1% was achieved with 3.3% initial sodium citrate under a current density of 40 mA cm^{-1}. Additionally, a decrease of voltage across AC by filling cation exchange resins restricted the migration of H^+ ions from AC to BC. A higher initial concentration of sodium citrate has an adverse effect on the recovery of citric acid. BC with a bipolar membrane (BPM) exhibited lower energy consumption and a higher recovery rate of citric acid. BMED appears to be a promising technology for recovering citric acid from fermented liquid.

1. Introduction

Citric acid can be used in many areas, such as the food, textile, chemical and pharmaceutical industries. There are two traditional ways to produce citric acid: fermentation and synthetic chemical reactions. The method of fermentation is the main technology in the field of citric acid production (Ali et al., 2016; Lotfy et al., 2007). The feedstock generally comes from renewable resources, such as silage, grains, syrups, molasses and cheese whey. Compared with synthetic chemical reactions, the products from fermentation are safer from an environmental perspective. The advantages are especially obvious for some organic acids that are difficult to produce via chemical synthesis. However, the fermentation of organic acids occurs at neutral pH to maintain the activity of the fermentation bacteria. As the acid output increases, the pH of the fermented liquid is continuously reduced, and thus, a strong base, such as NaOH, is typically used to increase the pH back to the optimum range. Therefore, a low concentration of sodium citrate instead of citric acid is obtained by the fermentation process.

To obtain citric acid, the technique of calcium salt precipitation-sulfuric acid acidification is usually adopted to convert sodium citrate into citric acid (Zhao et al., 2016). However, this conventional extraction process has some disadvantages, such as high energy consumption, large waste generation and low citric acid recovery. It is urgent to develop a new technology to directly obtain citric acid from sodium citrate in just one step instead of through an extraction process of calcium salt precipitation-sulfuric acid acidification to realize cleaner production of citric acid in industry (Vera et al., 2003; Xu, 2002).

Bipolar membrane electrodialysis (BMED) has many advantages over traditional chemical technologies for organic acid synthesis (Huang et al., 2007; Liu et al., 2015), including no gas or byproduct generation, a lower voltage drop, maximal energy utilization, space saving, and easier installation and operation. Most importantly, BMED can directly produce organic acid from organic acid salt via water splitting at the interface layer of a bipolar membrane. Currently, BMED has been used to recover some organic acids, such as sebacic, galacturonic, tartaric, lactobionic, succinic and salicylic acids, from fermented liquid (Gutiérrez et al., 2013; Liu et al., 2015; Molnár et al., 2010; Tran et al., 2015; Zhang et al., 2009, 2011). These studies indicate that BMED can be considered to be a prospective and cleaner technology for the production of organic acid.

However, there are several problems that need to be considered

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during the BMED running process. First, the recovery rate of acid needs to be further improved, especially for object acids with higher molecular weights (approximately 200 g mol^{-1} or more) (Novalic et al., 2000). For instance, the reported recovery of citric acid is less than 40% (Xu and Yang, 2002). Second, the energy consumption of citric acid production using the BMED process, which is up to 8.1–22.7 kwh·kg^{-1}, limits its industrial application to a certain extent (Wang et al., 2011). Third, electrolytes, such as Na_2SO_4, are usually fed into the base compartment (BC) to decrease the compartment resistance, which increases the cost of chemical consumption; of downstream treatments, such as separating the base solution from the electrolyte; and of wastewater discharge (Kai et al., 2009; Wang et al., 2011). Some studies have focused on the optimization of operation parameters, such as the current density and initial concentration of the solution, to enhance the recovery rate and reduce the energy consumption of the BMED process (Fu et al., 2014; Nikbakht et al., 2007). However, research regarding cell configuration improvements, especially packing ion exchange resins into the BC and acid compartment (AC), has rarely been reported.

In this study, three different cell configurations were designed by packing ion exchange resins into the BC or/and AC and replacing the bipolar membrane (BPM) with an anion-exchange membrane (AEM) in the BC. Purified water, instead of Na_2SO_4, was fed into the BC to obtain a pure base solution, and simulated sodium citrate solution was fed into the AC. Additionally, the influences of the density, initial concentration of sodium citrate and structure of the AC and BC on the recovery rate of citric acid were investigated in detail. Finally, a remarkable improvement was achieved in citric acid production by using the improved BMED.

2. Materials and methods

2.1. Materials

Analytical grade chemical reagents, including sodium citrate and sodium hydroxide, were used in this study. Bipolar membranes and homogeneous cation-exchange membranes, named BP-1E and Neosepta, respectively, were produced by ASTOM Co., Ltd., Japan, as well as the homogeneous anion-exchange membranes, named UTX-UIF-A, were obtained from Beijing Unisplendour Tongxing Environmental Technology Co., China. The characteristics of the membranes used in this study, as given by the manufacturer, are summarized in Table 1.

Strong acid macroporous-type cation exchange resins (CER) and strong alkali macroporous anion exchange resins (AER), D072 and D296, respectively, were manufactured by Chemical Plant of Nankai University, Tianjin, China. The AER was converted to the OH-type and washed by deionized water before use.

2.2. Experimental set-up

A schematic representation of the BMED stack configuration used in our study is displayed (Fig. 1). It consists of four compartments: the AC, BC, anode and cathode compartments. Two types of the AC were utilized in this study: either filled with two-layered nylon screens or with CER. In addition, two types of the BC were employed: one consisted of CEM and BPM and the other consisted of CEM and AEM.

Mixed-bed ion exchange resins with a volumetric ratio of 3:2 (CER to AER) were filled in the BC to decrease its electrical resistance. The effective surface area of each membrane was 220 cm^2. The thickness of the compartment with screen-filling or resin-filling was 1 mm and 6 mm, respectively. Two electrodes were made of titanium coated with ruthenium. A 0.5 mol L^{-1} NaOH solution was used as the electrolyte rinse circulating from anode to cathode with a flow rate of 6 L·h^{-1}. Three separated external cylinders were connected to the AC, BC and electrode compartment allowing for continuous recirculation by the diaphragm pumps. The volume of each cylinder was 2 L. A sodium citrate solution (Na_3Cit) (3.3%, 5% or 10%) was fed into the AC with a flow rate of 3.5 L·h^{-1} in the experiments. Purified water was fed into BC with an identical flow rate of 3.5 L·h^{-1}. A regulated power supply was used through which the voltage drop across the BMED stack could be directly measured. The voltage drop across BPM, AC and BC during BMED operation were measured with platinum (Pt) electrode pairs and digital multimeters (Doyen et al., 2013).

2.3. Analysis and testing

All experiments were performed under a constant current density. Volume changes of the solutions in three cylinders were recorded, and samples were taken at regular time intervals. The concentrations of citric acid and sodium hydroxide were determined by titration with standard sodium hydroxide and hydrochloric acid solutions with phenolphthalein as an indicator, respectively.

2.4. Evaluation of process performances

The BMED process performances were evaluated in terms of the recovery rate of citric acid (R), average current efficiency (η) and energy consumption (E), which were calculated by the following equations (Feng et al., 2007; Trivedi et al., 1997).

$$R = \frac{C_t \times V_t}{C \times V} \times 100\% \quad (1)$$

$$\eta = \frac{n(C_t V_t - C_0 V_0)VF}{NIt} \times 100\% \quad (2)$$

$$E = \int \frac{UIdt}{C_t VM} \quad (3)$$

where C, C_0 and C_t are the initial concentration of sodium citrate and citric acid at time 0 and t (mol·L^{-1}), respectively; V, V_0 and V_t are the initial volume (L) of sodium citrate and the circulated volume of the solution in the AC at time 0 and t (L), respectively; n is the ion absolute valence of organic acid; F is the Faraday constant; N is the number of cell pair ($N = 1$ in this case); I is stack current (A); t is the time in which the experiment was performed (s); U is the voltage across the BMED stack (V); and M is the molar weight of

Table 1
Main characteristic of the membranes used in the experiment.

Membrane	Type	Exchange capacity (mequiv·g^{-1} dry)	Thickness (mm)	Resistance(Ω·cm^2)
CEM	Strongly cationic	1.5–1.8	0.17	3.0
AEM	Strongly anionic	≥1.4	0.10–0.12	≤4
BPM	BP-1E	Water splitting voltage 1.2 V (Measured between 1 N NaOH and 1 N HCl, 10 A/dm^2 30 °C)		

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